

**TITLE: REMOVAL OF DRAG REDUCER ADDITIVE FROM LIQUID
HYDROCARBON FUEL USING ATTAPULGUS CLAY**

Cross-reference to Related Applications

5 [0001] The present application relates to U.S. Patent Application Serial No. 10/453,803, filed June 3, 2003, published as US-2004-0015034-A1 on January 22, 2004, pending. The present application also relates to U.S. Patent No. 6,599,337, issued July 29, 2003. Each of the foregoing references is incorporated herein by reference.

10 **Field of the Invention**

[0002] The application relates to a method for removing drag reducer additive ("DRA") from liquid hydrocarbon fuel using fresh attapulgus clay.

Background

[0003] DRA typically is added to flowing fluids in order to reduce the energy lost
15 due to friction, or drag, thus permitting the movement of more fluid at the same differential pressure. The resulting reduction in frictional pressure drop improves pumping efficiency, lowers energy costs, and increases profitability.

[0004] Unfortunately, whether in the virgin form or in the sheared or partially
sheared form, and despite the fact that it is intentionally added to certain fuels, drag
20 reducer additive still is a "contaminant" in liquid hydrocarbon fuels, and has the potential to cause a number of problems. Drag reducer additive is prohibited in aviation turbine fuels, although it has been observed as a contaminant due to accidental addition or other non-intentional means. The presence of drag reducer
additive in aviation turbine fuel may result in downgrading of the entire batch to non-
25 aviation kerosene or diesel fuel, both of which generally have less market value.

[0005] Viable methods of detecting and quantifying drag reducer additive in liquid hydrocarbon fuels commonly employ gel permeation chromatography, which is time consuming and expensive. Because of this, contaminated liquid hydrocarbon fuels often are used, despite the potential problems if drag reducer additive is present.

- 5 Contaminated aviation turbine fuels may be diverted to other uses or returned to a refinery for reprocessing, either of which results in additional expense.

[0006] Simple and inexpensive methods and materials are needed for removing drag reducer additive from liquid hydrocarbon fuels.

Summary

- 10 [0007] The present application provides a method for removing drag reducer additive ("DRA") from liquid hydrocarbon fuel. The method comprises: providing contaminated liquid hydrocarbon fuel comprising an initial concentration of DRA; contacting the contaminated liquid hydrocarbon fuel with a quantity of fresh attapulgus clay under conditions effective to produce decontaminated liquid
- 15 hydrocarbon fuel comprising a reduced concentration of the DRA; said fresh attapulgus clay being effective to remove about 10% or more of a target DRA when 1 g of the fresh attapulgus clay is added, with agitation, in increments of from about 0.02 gram to about 0.1 gram to 100 ml. of contaminated liquid hydrocarbon fuel comprising from about 8 to about 9 ppm of the unsheared target DRA.

Detailed Description

20 [0008] The presence of DRA in motor gasoline, even in sheared form, has caused increased intake valve deposits, plugging of fuel filters, and increased combustion chamber deposits. In jet engines, use of aviation jet fuel containing even sheared DRA has been shown to adversely affect the ability of the jet engines to reignite if a

flameout occurs. In diesel fuels, DRA may cause plugging of fuel filters and strainers and/or increased fuel injector deposits. DRA is prohibited in aviation turbine fuels, although DRA has been observed as a contaminant due to accidental addition or other non-intentional means. The presence of DRA in aviation turbine fuel may result in
5 downgrading of the entire batch to non-aviation kerosene or diesel fuel, both of which generally have less market value.

[0009] Attapulugus clay is used to remove polar contaminants from fuels, such as aviation fuels. Most DRA is relatively non-polar, and known systems comprising attapulugus clay have not demonstrated an ability to remove DRA from fuels.

10 **[0010]** Surprisingly, it has been found that “fresh” attapulugus clay does remove DRA from liquid hydrocarbon fuel.

[0011] “Fresh” attapulugus clay is defined as attapulugus clay which is effective to remove about 10% or more of a target DRA when 1 g of attapulugus clay is added in increments of from about 0.02 gram to about 0.1 gram, with agitation, to 100 ml. of
15 contaminated liquid hydrocarbon fuel comprising from about 8 to about 9 ppm of the unsheared target DRA. In a preferred embodiment, the fresh attapulugus clay is effective to remove about 20 % or more of a target DRA when 1 g of attapulugus clay is added in increments of from about 0.02 gram to about 0.1 gram, with agitation, to 100 ml. of a contaminated liquid hydrocarbon fuel comprising from about 8 to about 9
20 ppm of the unsheared target DRA.

[0012] Without limiting the application to a particular mechanism of action, the polar contaminants in liquid hydrocarbon fuels, particularly aviation fuel, are believed to selectively adhere to active sites on attapulugus clay in preference to DRA, which typically is relatively non-polar. As used herein, the phrase “used attapulugus clay”

refers to clay having active sites which are unavailable to bind DRA to the same extent as fresh attapulgius clay. Typically, "used attapulgius clay" has been exposed to liquid hydrocarbon fuel comprising contaminants which have a stronger attraction to the active sites of attapulgius clay than DRA.

- 5 [0013] Attapulgius clay is believed to comprise grains of fine sand, each of which is made up of even smaller particles that cling together to form a porous mass. These even smaller particles contain complex multicentered crystalline structures of oxides and hydroxides of magnesium, aluminum and silicon. Attapulgius clay generally comprises about 90 wt.% or more Fuller's earth and about 10 wt.% or less silica
- 10 crystalline (Quartz). The attapulgius clay generally comprises granules comprising a conglomerate of fundamental particles. A majority of the granules typically have a mesh size of from about 30 to about 90.

"Liquid Hydrocarbon Fuel"

- [0014] By "liquid hydrocarbon fuel" is meant any hydrocarbon that is liquid under
- 15 conditions of transport and/or storage. Suitable liquid hydrocarbon fuels include, but are not necessarily limited to those having a boiling range of from about 150 °F to about 750 °F, which may be used as a fuel. In one embodiment, the liquid hydrocarbon fuel is selected from the group consisting of liquefied natural gas (LNG), liquefied petroleum gas (LPG), motor gasoline, aviation gasoline, distillate fuels such
- 20 as diesel fuel and home heating oil, kerosene, jet fuel, No. 2 oil, residual fuel, No. 6 fuel, or bunker fuel. In a preferred embodiment, the liquid hydrocarbon fuel is selected from the group consisting of diesel fuel, jet fuel, aviation gasoline, and motor gasoline. In a more preferred embodiment, the liquid hydrocarbon fuel is jet fuel, at least in part due to the stringent requirements applicable to jet fuel and drag reducer

additive. The phrase “jet fuel” refers to both commercial jet fuel (Jet A, Jet A-1, and JET B) and military jet fuel, such as JP-4, JP-5, JP-8 and the like. “Contaminated liquid hydrocarbon fuel” refers to fuel comprising DRA.

“DRA”

5 [0015] DRA includes, but is not necessarily limited to polyolefin polymers comprising polyolefin moieties which are introduced into petroleum liquids for the purpose of reducing fluid flow drag. In a preferred embodiment, the drag reducer additive includes, but is not necessarily limited to, non-polar long-chain polyolefin polymers, generally referred to as “polyalphaolefins,” having a “peak” molecular
10 weight sufficiently high to allow the polymers to reduce fluid flow drag. Suitable polyalphaolefins are believed to have a molecular weight of about 1 million Daltons or more, more preferably about 10 million Daltons or more, most preferably about 25 million Daltons or more. The “peak” molecular weight refers to the peak that typically is measured as the drag reducer is eluted and detected during gel permeation
15 chromatography.

[0016] Suitable polyalphaolefins comprise polymerized linear alpha olefin (LAO) monomers having from about 2 to about 40 carbon atoms, preferably from about 2 to about 30 carbon atoms, more preferably from about 4 to about 20 carbon atoms, most preferably from about 6 to about 12 carbon atoms. An especially preferred
20 embodiment for a DRA which is effectively removable by the activated carbons and/or graphites described herein comprises two different LAO’s or more, preferably having from about 6 to about 12 carbon atoms, the number of carbon atoms of the two different LAO’s differing by 6.

[0017] Polyalphaolefins having relatively high molecular weights are required to

impart good drag reduction. Suitable polyalphaolefins “are made by a variety of processes, including but not necessarily limited to solution polymerization and bulk polymerization. Bulk polymerization is said to produce “ultra-high molecular weight polyolefin drag reducers [that] are significantly larger (molecular weight basis) than the best molecular weights made by solution polymerization.” See U.S. Patent No. 5,504,132. Preferred DRA’s for removal according to the process described herein are made by solution polymerization.

[0018] Without limiting the invention to a specific theory or mechanism of action, the very large polyalphaolefins made by bulk polymerization may be more difficult to adsorb onto and retain on the fresh attapulgus clay. In contrast, the polyalphaolefins made by solution polymerization may be more readily adsorbable onto the fresh attapulgus clay, and more readily retained by the removal agents.

[0019] Drag reducer additives are generally unsheared, partially sheared, or fully sheared. An additive that is fully sheared is one that is degraded in molecular weight to the maximum extent possible using high shear devices such as pumps, static mixers, etc. Commercially available drag reducer additives include, but are not necessarily limited to, CDR[®] Flow Improver REFINED POWER[™], and REFINED POWER II[™] manufactured by ConocoPhillips; EN-660 Flow Improver, manufactured by Energy 2000 LLC; and, FLO[®]XS and FLO[®]XL, manufactured by Baker Petrolite. In a preferred embodiment, the drag reducer additive is FLO[®]XS and equivalents thereof.

[0020] In another embodiment, the DRA comprises polar groups. Examples of suitable polar groups include, but are not necessarily limited to polar organic groups. Suitable polar groups generally comprise a moiety selected from the group consisting

of oxygen, sulfur, nitrogen, halogen, phosphorus, unsaturated carbon-carbon bonds, and combinations thereof.

[0021] The DRA may comprise other components besides the polyolefin moieties.

Examples of such components include, but are not necessarily limited to surfactant,

5 catalyst residue, other additives, and other byproducts from the production of the polymer. The polymer itself may contain other non-olefin monomer units as well.

[0022] When it is desired to remove DRA from a given fuel, one or more

attapulugus clay preferably is incorporated into a system for filtering the contaminated

liquid hydrocarbon fuel. The filter may be in any suitable form and may be installed

10 in a variety of locations.

[0023] Suitable locations for the filter system comprising the DRA removal agent

include, but are not necessarily limited to: at a refinery; between a refinery and a fuel

terminal; at a fuel terminal; between two different fuel terminals; between a fuel

terminal and a airport storage tank; at an airport storage tank; between a fuel terminal

15 and a tanker truck; at a tanker truck; between an airport storage tank and a tanker

truck; between two different tanker trucks; between a tanker truck and an engine, at a

fuel dispenser (such as a gasoline pump); between a fuel dispenser and a vehicle

comprising the engine; and, at the engine.

[0024] Before contact with the contaminated liquid hydrocarbon fuel, the fresh

20 attapulugus clay preferably is preheated to a temperature effective to remove adsorbed water (if any) without damaging the fresh attapulugus clay.

[0025] Due to the difficulty in providing for incremental addition and agitation in

most commercial situations, it may be preferred to simply pass the liquid hydrocarbon

fuel through a bed comprising the fresh attapulugus clay until the removal rate is so

low that the resulting “used” attapulgus clay must be replaced. In one embodiment, the filtering system provides for agitation of the DRA/fuel mixture as incremental additions of fresh attapulgus clay are added to the DRA/fuel mixture. This procedure is sometimes herein referred to as the “gradual addition and stirring” method or “Grad Add/Stir” method. This is a preferred method for more viscous hydrocarbon fuels such as jet fuel.

[0026] The application will be better understood with reference to the following examples, which are illustrative only:

EXAMPLE 1

10 [0027] The Grad Add/Stir method was used in this example. About 100 ml of jet fuel comprising about 8.36 ppm of sheared FLO[®] XS (manufactured by Baker Petrolite, sheared by mechanical agitation prior to its addition to the jet fuel) was stirred with a magnetic stir bar, to create a moderate vortex. Increments of about 0.02 to about 0.1 gram of fresh attapulgus clay obtained from Forcoven Products, Humble, 15 Texas, were placed in the agitating DRA/jet fuel mixture, while stirring, until a total of about 1.0 g of the fresh attapulgus clay had been added. The stirring was continued for approximately two to three minutes. The sample was allowed to settle for about 5 minutes. The fuller’s earth and silica crystalline were removed from the mixture by filtration with a Whatman 8 micron filter. The mixture was then tested for DRA 20 concentration. Over 20% DRA removal was achieved by exposure of the DRA/jet fuel mixture to the fresh attapulgus clay.

[0028] Persons of ordinary skill in the art will recognize that many modifications may be made to the present application without departing from the spirit and scope of the present application. The embodiment described herein is meant to be illustrative

only and should not be taken as limiting the application.